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KINETIC THEORY OF IMPERFECT GASES

AN EXTENSION OF KINETIC THEORY which makes it applicable to time-dependent processes in imperfect gases has resulted from recent statistical-mechanical investigations by the National Bureau of Standards into the theory of the Boltzmann equation.¹ This equation, the fundamental equation of the kinetic theory of gases, describes mathematically how the distribution of molecular velocities changes as a result of collisions among the molecules.

Carried out by Melville S. Green of the thermodynamics laboratory, this work is part of a larger study on the statistical mechanics of time-dependent phenomena. The study is being sponsored by the Office of Scientific Research of the Air Research and Development Command.

Previous formulations of the Boltzmann equation have taken into account only the effects of collisions involving a pair of particles. The present investigations, on the other hand, introduce additional terms which take account of simultaneous collisions among three or even larger numbers of particles.

Boltzmann derived the original equation with the help of a statistical hypothesis (the so-called *Stosszahlensatz*) about the number of molecule pairs that are in a position to collide during a given small time interval. Though highly plausible and supported by the many verified consequences of the Boltzmann equation, no obvious way of deriving the hypothesis from the principles of statistical mechanics has presented itself. Several efforts to give a more satisfactory treat-

ment have recently been made, notably by J. G. Kirkwood, H. S. Green, and N. Bogolyubov, all of which, like the present work, are limited to the realm of non-quantum dynamics. The Bureau study is indebted to these efforts, but it also exhibits significant formal and conceptual differences from them.²

Paradox of Irreversibility

In order to apply statistical-mechanical methods to time-dependent aspects of the kinetic theory of gases, it was first necessary to give at least a tentative answer to the question: How can a system of interacting mass points (which is the statistical-mechanical model of an imperfect gas) exhibit the universal tendency of bulk matter to approach a state of quiescence or thermodynamic equilibrium?

More generally, we encounter phenomena everywhere in the natural world which run their course for a time and then are over and done with. Yet these are to be explained by means of dynamical equations whose solutions are known to have a repetitive, if not strictly periodic, character.

On the one hand, it is known that the motion of an isolated system of mass points—the solar system is a good example—is repetitive, if not actually periodic. On the other, time-dependent processes in bulk matter—examples are fluid motion, chemical reactions, heat conduction, and diffusion—all lead, possibly through a series of ever-decreasing oscillations, to a

final state from which there is no tendency to return towards or to repeat the initial state. The question, then, is how time-dependent phenomena in the statistical-mechanical model of an imperfect gas, which is of the same type as the solar system, can nevertheless exhibit the approach to equilibrium characteristic of all kinds of bulk matter including imperfect gases.

Various mathematicians and physicists have considered this problem and, in the course of many years, a number of solutions have been proposed. The present derivation of the Boltzmann equation lends support to one of these solutions. According to the latter, irreversible behavior, like many of the laws of equilibrium statistical mechanics, is an approximation that holds strictly only in the limit of large volumes and numbers of particles. When the number of isolated mass points is as large as it is in bulk matter (i. e., in portions large enough to be conveniently observed) the times of repetition are extremely long. Indeed, for a system containing as many particles as, say, a drop of water, the time intervals between recurrences of similar states are enormously longer than the time scales of ordinary experience. Thus, the statistical-mechanical model of an imperfect gas need not exhibit repetitive processes—for all practical purposes.

Results

Once the application of statistical-mechanical methods to the theory of imperfect gases has been made, it becomes possible to carry over ideas from the equilibrium (time-independent) theory of imperfect gases. This can be done, for instance with the technically very useful virial expansion of the equation of state. The virial expansion is a representation of the pressure as a series of powers of the density or inverse volume. The successive coefficients of this power series can be obtained by statistical-mechanical methods from the interaction energy of groups of 2, 3, and more molecules.

Four of the types of collision events among three molecules considered in a statistical-mechanical study of imperfect gases. (A) Successive binary collisions; molecules 1 and 2 collide, then molecule 3 collides with molecule 2. (B) Intercepted binary collision; molecules 1 and 3 move toward collision with each other, but instead molecule 1 is deflected by a collision with molecule 2. (C) Genuine triple collision; contact between molecules 1 and 2 is effectively simultaneous with that between molecules 2 and 3. (D) Succession of binary collisions which is effectively a triple collision; molecules 2 and 1 collide, then 2 and 3, then 2 and 1 again. Types A and B are taken into account in previous formulations of the Boltzmann equation. Only types C and D enter into the triple-collision term of the equation as derived in the Bureau study. In the hard-sphere model, type C has negligible probability of occurrence but type D occurs with considerable frequency. In a more realistic model of an imperfect gas, neither type C nor type D can be neglected.

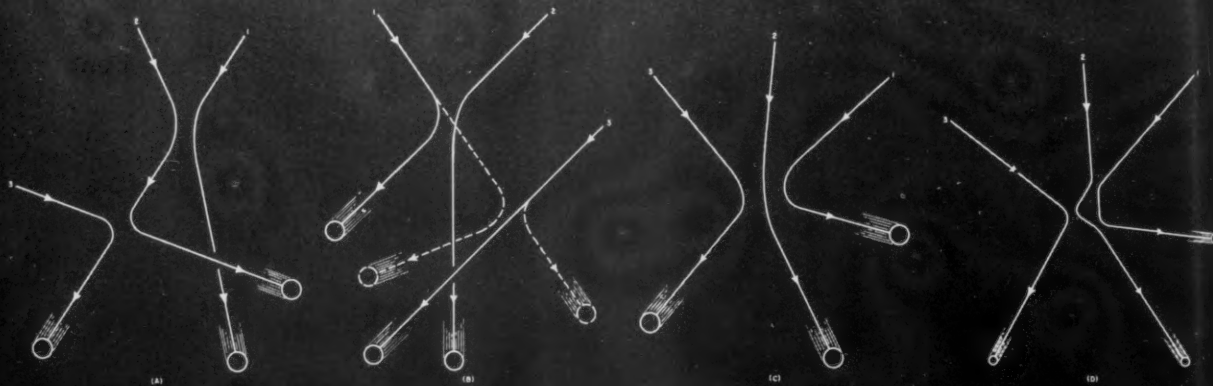
Similarly, in the time-dependent theory of imperfect gases, expansions in powers of the density can be set up for a number of properties—the molecular velocity distribution functions and, ultimately, the transport properties such as viscosity, heat conductivity, and diffusion. Here the successive coefficients are determined not only from the energy of interaction but also from the complete dynamics of interaction—that is, from an analysis of collisions involving 2, 3, etc., molecules.

The problem of determining the coefficients in a density series for the transport properties is inherently more difficult than the analogous problem for the equation of state. It is planned, however, to carry the present investigation forward to the extent of computing the effect of increased pressure (or density) on the viscosity, thermal conductivity, and other transport properties of monatomic gases. These computations will involve the dynamics of the simultaneous collision of three molecules.

The results of the investigations have applications to the theory of other effects in gases brought about by or involving intermolecular collisions. An example is the pressure broadening of lines in microwave and other spectra. The results are most useful in the pressure range extending up to a few hundred atmospheres. At higher pressures it is no longer possible to analyze the effect of density on the transport or other properties in terms of multiple simultaneous collisions.

¹ For further technical details, see The Boltzmann equation from the statistical mechanical point of view, by Melville S. Green, *J. Chem. Phys.* **25**, 836 (Nov. 1956); and Statistical mechanics and the Boltzmann equation, by Melville S. Green, *Proceedings of the Brussels Colloquium on Transport Properties in Statistical Mechanics*, Academic Press, New York (in press).

² For remarks on the relation of the present investigation to other recent work on this problem, see the first reference in footnote 1.



RF Voltmeter Calibration Consoles

THREE SPECIAL CONSOLES have been developed by M. C. Selby, L. F. Behrent, and F. X. Ries, to calibrate rf voltmeters for science and industry in the newly established Calibration Center of the Radio Standards Laboratory, at the Bureau's Boulder Laboratories.

With these consoles, very accurate calibrations can be performed in a fraction of the time heretofore required. RF voltmeters will be calibrated for any practical voltage level starting with 0.2 v at discrete frequencies of 30, 100, 300, 1000 kc, and 5, 10, 30, 100, 300, 400, 500, and 700 Mc.

The major components comprising a complete calibrating system at each frequency are of rf sources, reference voltage standards, filters, impedance matching networks, automatic level controls, a manual level control, and protective and indicating circuits.

Salient feature of the system is the application of the AT voltmeter, the most stable rf-voltage reference standard known to date.¹ This voltmeter can reproduce calibration data to ± 1 percent or better over a period of 1 year or longer. To make good use of such a standard, sources of error in the auxiliary components must be kept to a minimum.

The operation of the system is as follows: Seven fixed-type AT voltmeters, calibrated for levels of 0.2 to several hundred volts, are mounted on the underside of a special metallic ground plate that permits rapid connection of an "unknown" voltmeter on the top side of this plate. The input planes of the unknown and of the AT voltmeter are located very close together across the terminals of a coaxial cable imbedded in the plate. The cable furnishes rf voltages to the two voltmeters thus connected in parallel with essentially no connecting leads. This eliminates errors normally introduced by standing waves.

The rf voltages originate in constant-temperature crystal-controlled oscillators. These voltages are amplified, filtered to reduce all harmonics at least 60 db below the fundamental, and are fed via proper matching networks to the voltmeters. Overload circuits and relays protect the thermoelements of the AT voltmeters from being accidentally overloaded. An automatic amplitude stabilizing circuit keeps the rf voltage, applied to the voltmeters, constant to 0.1 percent over a period of 1 hour or longer. Errors caused by voltage drifts during observations are thus made negligibly small. The rf voltage levels are indicated on a common panel indicator and are translated into voltage values

by the use of line charts obtained when the AT voltmeters are calibrated in terms of NBS primary standards.

Three of the AT voltmeters covering values to 20 volts each have a nominal 50-ohm input impedance. These are calibrated and used at two discrete frequencies. Two additional higher-input-impedance AT voltmeters are added for each of the two frequencies at high voltage levels. Thus a total of seven AT voltmeters furnish facilities for the complete voltage range



One of three rf-voltmeter consoles developed to calibrate all types of voltmeters. Twelve discrete frequencies to 700 Mc are used and all practicable voltage levels of 0.2 volt and higher are available. The probe of an "unknown" voltmeter is connected in parallel with a standard AT voltmeter (inside console). Standard-voltage levels are indicated on the mirror-type panel instruments. The indications of the latter are translated into rf voltage values by means of the line charts and sliding magnifying index lenses shown on the front panel. Reproducibility is 1 percent or better over a period of 1 year or longer.

at two frequencies. The apparatus for the 2 frequencies is assembled into 2 cabinets and is combined with another similar apparatus for 2 other frequencies to form a 4-frequency console. Three consoles will cover the entire frequency and voltage range indicated above. The combinations and number of consoles were chosen to allow simultaneous calibration work on 3 to 6 voltmeters.

¹ Stable radiofrequency voltmeters, *NBS Tech. News Bul.* 40, 29 (February 1956).

New Film Announced

ASSIGNMENT—WEIGHTS AND MEASURES

A new film, which tells the story of how weights and measures supervision affects the average American family, has been announced by the National Conference on Weights and Measures. Produced by the Conference through the cooperation of the Bureau, the

film is in color and sound, and runs for 18 minutes. For information about the loan or purchase of this film, write to the Secretary, National Conference on Weights and Measures, National Bureau of Standards, Washington 25, D. C.

Warning Light for Aircraft Panels

A COMPOSITE EYE-LEVEL WARNING light for aircraft panels has been developed by T. O. Twist and R. S. Rinkinen. Devised for the Navy Bureau of Aeronautics, the small, compact lighting fixture combines six indicating lamps which warn the pilot, by appropriately illuminated legends, when any essential part of the aircraft is not operating properly. The device is sufficiently small to be mounted on the cowling above a cockpit instrument panel, close to the pilot's normal line of sight without interfering materially with his vision.

For many years the National Bureau of Standards has been conducting a program of standardization in aircraft lighting for the Navy Bureau of Aeronautics. Recently, because of the rapidly increasing number of types of warning lights being furnished with newly developed planes, the Navy requested NBS to develop a standard composite warning light and to prepare a specification for it.

In modern military aircraft the control and instrument presentations are becoming increasingly complex while available space for locating them is decreasing. Ordinarily warning lights are designed as individual units and, except for fire warning lights, are mounted wherever space is available. The miniature composite light was designed both to conserve space and to centralize warning lights within the pilot's field of vision in the cockpit.

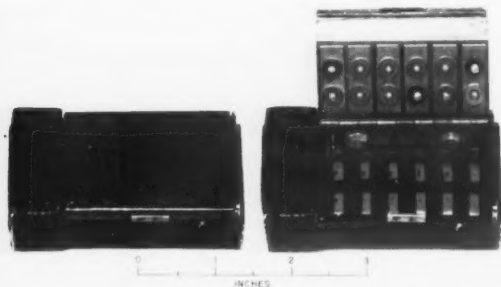
Two prototype units were constructed and were used

assembly by a common hinge. The lamps in the hinged sections make contact with spring strips of phosphor-bronze mounted on a fiber insulating plate on the opposite side of the box. The second model has a push-to-test bar at one end which can be used to test all indicator lamps simultaneously. Both models can be mounted flush to existing aircraft instrument panels and are arranged so that individual lamps can be changed in flight.

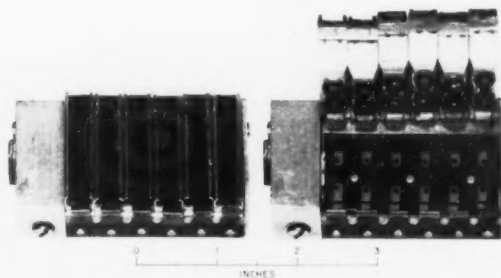
The two prototypes effectively demonstrate the advantages of grouped warning light fixtures over separate visual indicators in size, weight, and mounting simplification. Thus over-all weight, 4.5 oz., as well as the panel space occupied, is about equal to that now required by three of the separate indicator lights. Further size and weight reduction may be expected through application of production methods of manufacture.

The units were designed to operate from 28 volts ac or dc. Two type 327 subminiature lamps are used for each indication. The electrical circuit which provides current to the lamps was fabricated of thin, narrow strips of phosphor-bronze. In production printed circuit techniques could be substituted for the phosphor-bronze conductors used in the prototypes.

Both positive and negative lead wires for each indicator were required to be insulated from the indicator mounting case. Thus, the push-to-test switch had to interrupt six pairs of wires during lamp test. Since



Prototype model of small, compact warning light fixture developed for aircraft panel use. Two type 327 subminiature lamps illuminate the legend in each glass panel in the hinged front of the assembly. The push-to-test bar at left is used to test all lamps simultaneously.



Second prototype of the composite warning light. In this model the push-to-test bar is absent and the indicator sections are hinged individually.

by the Bureau of Aeronautics as a basis for a procurement specification. Each consisted of a small metal box ($3.1 \times 1.5 \times 1.0$ in.), one side of which opens on hinges. The warning lights are mounted in the hinged side. One prototype has six individually removable hinged indicator sections while the other has six fixed indicator lights fastened to the main body of the as-

sembly. The available space ruled out the use of commercial 6-pole double-throw switches, it was necessary to design a special type of switch. In this switch the moving element consists of a thin plate of rigid insulating fiber material carrying two parallel rows of metal balls which are exposed on either side of the plate. The moving element is sandwiched between two additional fiber plates, each of which carries two parallel sets of six individual contacts spaced to match the balls in the

center plate, and two parallel bar contacts extending the width of the plates. The center plate is attached with suitable spring loading to the actuating bar.

Normally, contact is made between the individual contacts on the outside plates through the metal balls on the center plate. When the actuating bar is de-

pressed, the balls are transferred from the individual contacts to a lower position where they make contact with the bars, which are common to all the lamps. This switch is relatively simple to fabricate, requires no complicated adjustments, and permits numerous contacts to be made within a small space.

Wax-Electrolyte Batteries

AFUNDAMENTAL INVESTIGATION of the chemical and electrical properties of batteries made with solid wax electrolytes is now under way at the Bureau. This new field of battery research is expected to provide information of value not only in fabricating batteries but in understanding the phenomena that take place in wax electrolytes subjected to electric fields.

The study is being conducted by R. E. Wood¹ of the electrochemistry laboratory at the request of the Diamond Ordnance Fuze Laboratories, Department of the Army. The immediate objective is to obtain information that can be used in constructing batteries for specific ordnance applications.

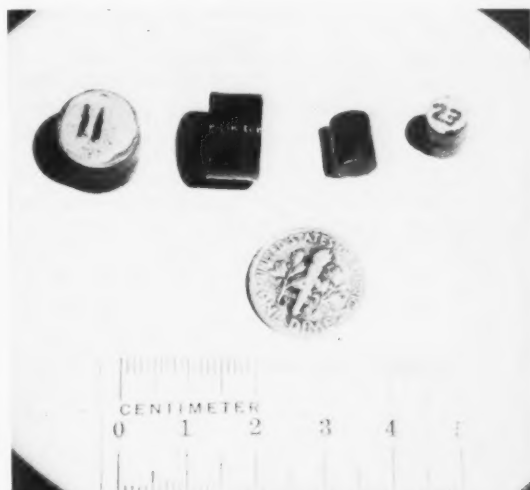
In the course of the work, a low-current punched-cell battery has been developed which has a waxy electrolyte consisting mainly of solid polyethylene glycol. This battery is not only compact and easily constructed but produces high voltage even after long-term storage. It is stamped from a three-layer sandwich consisting of a zinc sheet, a conductive vinyl film, and between these two layers, a separator impregnated with a zinc chloride-polyethylene glycol mixture. The separator is coated on one side with manganese dioxide. Among other applications, the battery is expected to prove useful in maintaining a charge on a capacitor and in producing a grid-bias voltage for radio tubes.

Several 25-cell wax-electrolyte batteries have been constructed at the Bureau. They are 0.3 inch in length and have an electromotive force of 37.5 volts. Two different sizes of batteries were made: One is 0.25 inch in diameter weighing 0.05 ounce, with a short-circuit current of 3×10^{-8} ampere, while the other is 0.5 inch in diameter, weighing 0.2 ounce, with a short-circuit current of 3×10^{-7} ampere at ordinary temperatures.

Construction of the cell is begun by etching a sheet of zinc to increase adherence to the waxy polyethylene glycol. A solution of melted glycol, with zinc chloride dissolved in it, is equally divided and manganese dioxide is added to one portion. A piece of filter paper, the same size as the zinc sheet, is placed on a hot plate to maintain a temperature a little higher than the melting point of polyethylene glycol. One side of this is painted with the polyglycol wax-zinc chloride mixture not containing MnO_2 , and the other side is painted with the wax mixture containing MnO_2 .

Following the coating of the filter paper, it is placed between the zinc sheet and a conducting plastic one, which is somewhat larger than the zinc sheet. After the sandwich-cell is squeezed to expel any excess wax, it is cooled, washed, and trimmed. Disks, either 0.5

or 0.25 inch in diameter, are punched from this sandwich. Twenty-five of these cells or disks are stacked in series in a press, and the cylindrical surface is lacquered. The twofold purpose of the lacquering is to seal the edges of the cells and to hold the cells together in the battery.



The actual size of the compact, high-voltage batteries is demonstrated by comparing them in size to a dime. Diameters of these 25-cell batteries are 0.5 and 0.25 inch, respectively.

To find out how long batteries could be kept without appreciable loss of voltage, the punched-cell batteries were stored at room temperature in desiccators containing silica gel. Results show changes of only a few percent in the emf's of a large majority of the batteries after 3 years of storage.

Although different molecular weights of polyethylene glycol were initially used, there are hardly enough data on glycol electrolytes to permit well-founded generalizations regarding the effect of molecular size on short-circuit current. The 2000-, 4000-, 6000-, and 9000-molecular weight glycol batteries with filter paper separators all show internal resistances increasing with molecular weight, except for the 6000-type, which falls into the same short-circuit current range as the comparable 4000-type one.

There is, however, a clear indication with respect to separator materials used. Either a rough quantitative

Materials used in making small punched-cell, polyethylene glycol batteries. Economical and easily constructed, the miniature wax-electrolyte batteries produce high voltage using a low current. In the foreground, left to right, are the zinc chloride powders, the manganese dioxide, and the polyethylene glycol powders; in the background are the zinc roll and the conductive plastic sheet. All are standing on the oversized filter paper separator which will be coated with ZnCl₂-glycol mixture.



grade of filter paper or one of two different thicknesses of a nonwoven fabric were used as separators. The latter are tough matted sheets of rayon with much more open and less homogeneous structures than filter paper. The more open-structured the separator, the lower was the internal resistance. The short-circuit currents from batteries with separators of the most open-structured materials were greater by a factor of 4 or 5 than those of batteries with filter paper separators. During 3 years of observation, no significant differences in emf developed between these two groups of batteries.

The useful temperature range for the wax-electrolyte batteries depends on shelf life and current requirements. The shelf life would probably be greatly decreased if the battery were heated above the melting point of the electrolyte, which is around 45° C for the 4000-type polymer, while the lower temperature limit of the useful range for this type electrolyte would be about 0° C.

To achieve a lower internal resistance and an extended useful temperature range, batteries with a gel electrolyte rather than a waxy one were made. Ethylene glycol or lower liquid polymers were absorbed by a synthetic, water-sensitive gum to form tacky gels which retained their stickiness over an extended tem-

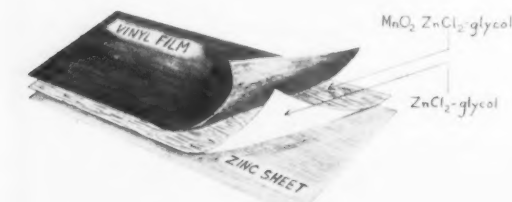
perature range. It was shown that the resistance ratios of the two types of cells vary only a little with temperature over the range studied, though the actual resistance of the wax cell was much greater than the gel cell at the same temperature. The gel cells, having a considerable lower limit in their useful temperature range than the wax ones, can also be heated to rather high temperatures with no apparent damage. The shelf life, however, of the gel batteries is comparatively short, probably because of intercellular leakage.

¹For further details, see Punched-cell batteries with polyethylene glycol electrolytes, by Reuben E. Wood, *J. Electrochem. Soc.* **103**, 417 (August 1956). See also U. S. Patent No. 2,762,858.

TABLE 1. Representative data on 25-cell, polyethylene glycol punched-cell batteries

Group	Number of batteries in group	Electrolyte (average molecular weight of glycol)	Separator	Age range	EMF range	Short-circuit current range
½ in. (1.270 cm) batteries with powdered MnO₂						
				Months	Volts	amp×10 ⁻³
1	4	4000	FP	20	36 to 37	30 to 50
2	4	6000	FP	17 to 18	33 to 36	25 to 30
3	8	4000	FP	16	35 to 37	20 to 30
4	4	2000	FP	16	35 to 36	45 to 60
5	2	4000	Munsing paper	15	33 to 34	60
6	4	9000w	FP	15	32 to 34	5
½ in. (1.270 cm) batteries with electrodeposited MnO₂						
7	5	4000	R-25-F	13	37 to 38	140 to 190
8	5	4000	FP	13	37 to 38	30 to 45
9	5	4000	R-45-F	13	21 to 33	50 to 110
10	1	4000	Nylon	12	35	80

Under "separator," "FP" means a "qualitative or rough quantitative" grade filter paper while "R" stands for tough matter rayon sheets of nonwoven fibers. "F" is a soft grade, while "25" and "45" are numbers approximately proportional to thicknesses. When only 1 number is listed in the "Age range" column, it means all the batteries in the corresponding group were within ½ month of the age listed.



Each cell of the wax-electrolyte battery is made from a three-layer sandwich. The sandwich is composed of a zinc sheet, a conductive vinyl film, and, between these two layers, a separator impregnated with the ZnCl₂-glycol mixture and coated with manganese dioxide on one side.

Estimating Heats of Combustion of Aircraft Fuels

THE BUREAU has developed a convenient, reliable method for estimating heats of combustion of aviation gasolines. The method does not require elaborate calculations nor extensive analytical work, but is based on an empirical equation relating heat of combustion to the proportions of various hydrocarbon types present. Adaptable for use by oil refineries, the procedure is expected to prove useful in checking aviation gasolines for conformance to military specifications.

Jet-propelled aircraft—both manned and unmanned—require increasingly better performance of liquid propellants. Hence, military standards for fuels are becoming more exacting. One of the specifications stipulated in military contract bids is a highly accurate value for the fuel's net heat of combustion, but this property can be measured only by complex and expensive apparatus not available to most refineries. Seeking a convenient means for estimating net heat of combustion, George T. Armstrong, Ralph S. Jessup, and Thomas W. Mears have been investigating the relationships between net heat of combustion and other more easily measured properties of aircraft fuels.

Investigations sponsored by the Navy Bureau of Aeronautics showed that the net heat of combustion of a well-defined class of fuels can be expressed as a linear function of the product of the aniline point¹ of the fuel in degrees Fahrenheit and the gravity of the fuel in degrees API—in other words, the aniline-gravity product. However, a different equation usually is necessary for each class of fuel. Also, it was clearly shown that the net heat of combustion is a function not only of the aniline-gravity product but of other variables as well.²

In recent work for Wright Air Development Center, Department of the Air Force, measurements of the following properties were made on 33 grade 115/145 gasolines and 7 grade 100/130 gasolines: (1) Heat of combustion, (2) the aniline-gravity product, (3) hydrogen content, and (4) composition in terms of the various hydrocarbon types.³ Data obtained from these measurements were used to derive empirical relations between net heat of combustion and the other properties given above.

An approximate linear relationship was found in each case; but the accuracy of the estimated heat of combustion was much better in some relationships than in others. This is apparent from the standard deviation of the measured heat of combustion from that calculated for each measured physical property as listed below:

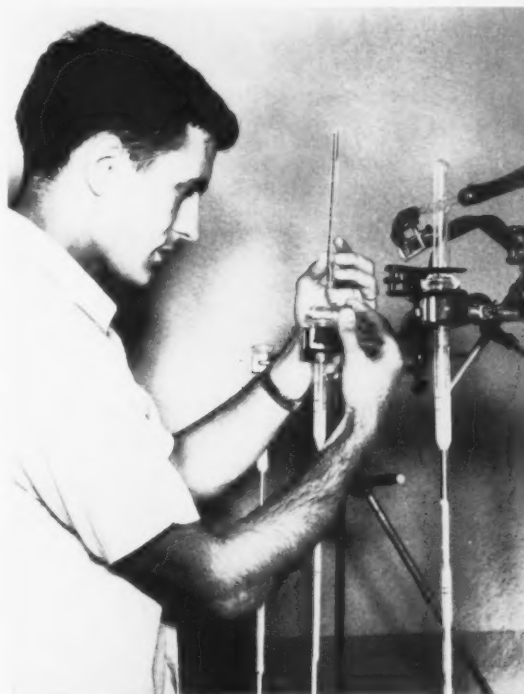
	Percent
Aniline point.....	0.14
API gravity.....	.26
Aniline-gravity product.....	.12
Hydrogen content.....	.14
Composition in terms of hydrocarbon types.....	.07

These percentages indicate that the most accurate means so far investigated for estimating heat of combustion of aircraft fuel is the method based on the composition of the fuel in terms of hydrocarbon types.⁴

In arriving at this method, the fuels first were analyzed by a standard ASTM procedure of silica gel adsorption into saturates, olefins, and aromatics. The saturate fractions were further analyzed for paraffins (P), naphthenes (N), olefins (O), and aromatics (Ar). The equation which relates net heat of combustion [$Q_p(\text{net})$], in British thermal units per pound, to weight percent of the hydrocarbon types is as follows:

$$Q_p(\text{net}) \text{ Btu/lb} = 190.892(P) + 183.80(N) + 176.73(O) + 172.65(\text{Ar}).$$

It may be assumed that in a fuel having boiling range and other properties limited by specifications such as



Chemist analyzing aircraft fuel into its various hydrocarbon types by a standard ASTM test. This is one step in a method used to estimate the net heat of combustion of an aircraft fuel from the hydrocarbons present in the fuel.

those required for aircraft fuels, the hydrocarbons of which the fuel may be composed will be limited to a small group of related compounds within each hydrocarbon type. Therefore, the range of possible values of heat of combustion would be considerably less than in fuels that do not measure up to the specifications. As a consequence, mixtures within such a group of compounds will have a characteristic heat of combustion per unit weight which will not vary much from one mixture to another. Thus, it might be expected that the heat of combustion per unit weight of a fuel would be a linear combination of the percentages by weight of the hydrocarbon types as shown in the preceding equation. It should be pointed out, however, that this is still an empirical equation which is sensitive to factors that vary from one class of fuel to another.

The complete calculation of the heat of combustion of a fuel by analyzing all of its molecular components

and averaging their heat of combustion is theoretically possible, but such an experiment is not presently feasible. On the other hand, the Bureau's method is well within the testing capacity of most oil companies' laboratories.

¹ Aniline point is the minimum equilibrium solution temperature for equal volumes of aniline and of sample.

² For further technical details, see Relation between net heat of combustion and aniline-gravity product of aircraft fuels, by Ralph S. Jessup and Joseph A. Cogliano, *ASTM Bull.* No. 201, p. 55 (1954), and Net heat of combustion of AN-F-58 aircraft fuels, by Simon Rothberg and Ralph S. Jessup, *Ind. Eng. Chem.* **43**, 981 (1951).

³ These gasolines were selected from over 200 samples submitted by 39 oil refineries.

⁴ Net heat of combustion of aviation gasoline and its correlation with other properties, by George T. Armstrong, Ralph S. Jessup, and Thomas W. Mears, *I&EC's Chemical and Engineering Data Series* (in press).

New Color Scale for Petroleum Products

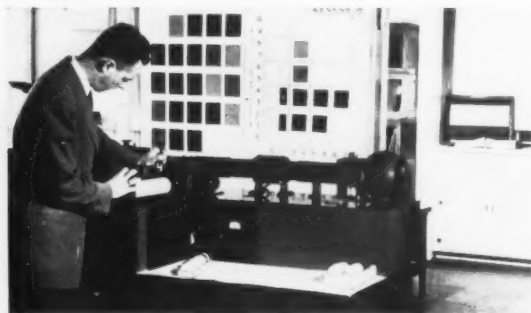
A NEW COLOR SCALE to measure the degree of refinement of petroleum products has been devised by the Bureau in cooperation with the American Society for Testing Materials. Glass standards to match the color specifications of the new scale are now being made in this country, and when these standards are put to use, the difficulties and discrepancies inherent in the present method of color-grading petroleum will be largely overcome. Manufacturers and purchasers of petroleum then will have a uniform guide to measure the quality of a product.

Crude oil is black and nearly opaque; during the refinement process the color changes through dark red, orange, lemon yellow, and pale yellow to crystal clear. In this manner, the degree of refinement is determined by the color of the product. Since 1923, it has been customary to measure and specify the color

of petroleum by means of the ASTM (American Society for Testing Materials) Union Colorimeter.¹ This instrument contains a series of 12 glass standards mounted in a vertical slide that may be raised or lowered to permit visual comparison of any one of the glasses with a petroleum sample placed in the colorimeter. Partially refined petroleum is bought and sold at prices determined for the most part by these 12 glass color standards.

The original set of glasses, obtained from abroad and maintained by ASTM, imperfectly duplicates by nonuniform steps the range of oil colors, and working sets of similar glasses are used by most oil refineries. During recent years, inaccuracies obtained upon occasion in color-grading petroleum by these standards gave impetus to a search for other means. A research group within ASTM's Committee on Petroleum Products and Lubricants enlisted the aid of the Bureau. So colorimetric specifications for a new set of glass color standards, adjusted precisely to the average color range of petroleum products, were developed by D. B. Judd, L. Plaza, and M. A. Belknap of the photometry and colorimetry laboratory.² On the new scale the color range was established in 16 uniform steps.

Three outstanding defects of the original glass color standards were the following: (1) The color scale was not defined in fundamental terms with stated tolerances, and working sets of glasses held by dealers deviated from the master set; (2) the glasses failed to show precisely the average colors of petroleum in various stages of refinement, particularly in the lemon yellow to orange range; (3) the 12 steps on the scale were perceptually nonuniform so that inaccuracies occurred when a sample of petroleum was compared visually with a standard nearly matching it. As a result of these defects, when a purchaser of partially refined petroleum



A spectrophotometer is used to calibrate glass color standards. As partially refined petroleum is bought and sold at prices largely determined by color, similar standards are maintained by most oil refineries to color-grade petroleum.

which was specified as color No. 3 on the color scale, found by his own measurement that it was really color No. 3½, he was forced at considerable expense to refine his purchase to the desired degree.

In setting up the new color scale, the Bureau measured the colors of 49 samples of petroleum in the pale yellow to orange range. Based on these measurements, a relocated and respaced color scale was calculated. The new scale with tolerances is specified in terms of spectral transmittances and the CIE standard observer.³ As soon as the scale was submitted to the ASTM Committee, the Committee's research group directed its effort toward finding reliable sources of supply in this country for sets of glass color standards to fit the specifications.

With the financial support of the Committee, the Bureau, in cooperation with a supplier of glass color standards, designed a set of glasses meeting the desired tolerances. Glass samples submitted by two other companies were measured at the Bureau. These measurements indicate that procurement of satisfactory dupli-

cate color standards from various suppliers, though not easy, is feasible.

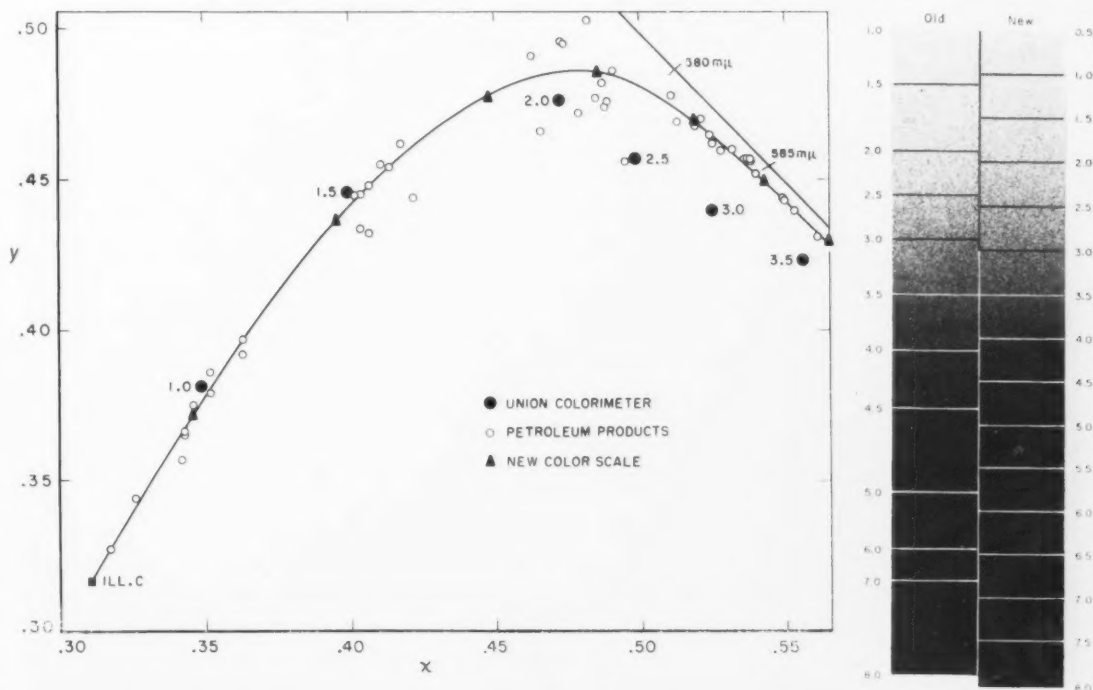
In April 1957 the research group of the Committee approved a new tentative method for color-grading petroleum products based on the revised color scale.⁴ This decision was made after extensive cooperative tests showed that agreement between laboratories using the revised color scale was possible. Formal approval of the new method by the Committee on Petroleum Products and Lubricants was announced at the recent ASTM annual meeting in Atlantic City.

¹ Tentative method of test for color of lubricating oil and petrolatum by means of ASTM union colorimeter, ASTM designation: D 155-45 T.

² A suggested relocation and respacing of the union colorimeter scale for lubricating oil and petrolatum, by Deane B. Judd, Lorenzo Plaza, and Marion A. Belknap, J. Research NBS 44, 559 (1950) RP2103.

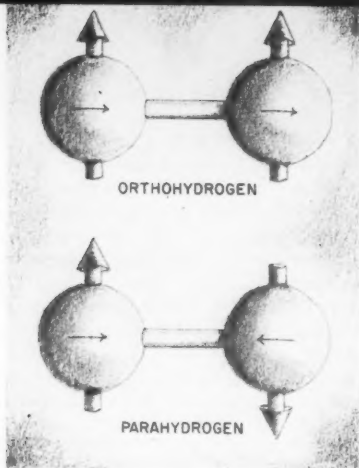
³ For purposes of colorimetric computation, this is an average observer, statistically determined by the International Commission on Illumination (Commission Internationale de l'Eclairage).

⁴ Tentative method of test for measuring the color of petroleum products, ASTM designation: D 1500-57 T.



Left: Curved line on this (x,y)-chromaticity diagram runs from a point representing average daylight (ILL. C) to a region near the spectrum locus at 585 millimicrons and beyond. The curved line corresponds closely to the average chromaticities of the petroleum products in the lemon yellow to orange range, and reflects the relocation of the colorimeter scale. The black triangles on the line correspond to the first seven colors on the new scale. Right: Color scale used in the ASTM Union Colorimeter compared with the revised color scale recommended by the Bureau. Note the uniform spacing of the new scale.

CATALYST FOR PARA



AN UNUSUALLY EFFECTIVE CATALYST for converting ortho- to parahydrogen, developed by the Boulder (Colorado) Laboratories of the National Bureau of Standards, greatly simplifies the problem of liquid hydrogen storage. The research was conducted by the Cryogenic Engineering Laboratory as part of its general program to improve methods of efficient production and storage of liquid hydrogen and other cryogenic (low-temperature) materials and to facilitate their economical large-scale utilization. The present result was obtained in a project sponsored by the U. S. Atomic Energy Commission.

The fact that hydrogen consists of two kinds of molecules, known as orthohydrogen and parahydrogen, considerably complicates the problem of storing liquid hydrogen. This is because the orthomolecules are unstable at low temperatures and change into paramolecules, liberating heat energy in the process and causing wasteful evaporation. Before the development of conversion catalysts, the problem could be met only by the use of special refrigeration equipment to remove the heat generated during the relatively long time needed for the orthohydrogen to change to parahydrogen.

The development of effective catalysts has made possible the reliable, continuous production of liquid hydrogen having a high para content. The necessity for cumbersome and expensive refrigeration equipment to absorb the heat of conversion at the storage site is eliminated since liquid parahydrogen is transferred to storage directly from the liquefier where the catalysis takes place. Thus, efficient storage of the stable liquid parahydrogen can be accomplished by providing well-insulated storage vessels to protect the liquid from heat transferred from the environment.

Two Kinds of Hydrogen

The two types of hydrogen molecules are distinguished by the orientations of their nuclear spins. Each hydrogen molecule is made up of two atoms, and the positively charged proton in the nucleus of each atom has associated with it a field which can be mathematically described as being caused by spinning of the proton itself. Since there are two atoms and therefore two "spinning" protons in each molecule, the two protons can be visualized as rotating either in the same direction or in opposite directions; that is, the "spins" can be either parallel or antiparallel. In the parallel case there exists an orthohydrogen molecule; in the antiparallel case, a parahydrogen molecule.

There is also a difference in the energies associated with these two molecular varieties. The orthohydrogen molecule has "end-over-end" rotational energy, even at the absolute zero of temperature, while parahydrogen has negligible rotational energy at the boiling temperature of hydrogen. Thus a change from orthohydrogen to parahydrogen will result in a release of energy as the molecule goes from the first to the zero rotational energy level.

If one (but not both) of the atomic nuclei in a hydrogen molecule reverses its direction of rotation, it means that the molecule has changed from orthohydrogen to parahydrogen, or vice versa. A change of this kind cannot take place unless the molecule obtains (from other molecules or from some outside source) sufficient energy to get it past the "energy barrier" which confines it to its existing energy level. These conversions are continuously taking place among the millions of molecules in a volume of hydrogen gas or liquid, but eventually an equilibrium is reached when

Above: Simplified schematic representation of the two types of hydrogen molecules. Each type consists of 2 hydrogen atoms (spheres) connected by a covalent bond (connecting bar). Light arrows indicate direction of nuclear spin; heavy arrows penetrating spheres show direction of spin axis. In orthohydrogen, the less stable type at lower temperatures, the spin axes point in the same direction; in parahydrogen the axes are directly opposed. *Right:* The operation of the catalyst for ortho-to-para conversion. Catalyst is a porous ferromagnetic material, hydrous ferric oxide, through which normal hydrogen (75 percent ortho, 25 percent para) is made to pass. The magnetic field within the small pores, one of which is represented here (dotted lines are lines of magnetic force), varies rapidly from one point to another; and the inhomogeneous field interacts with the magnetic moments of the hydrogen atoms and produces internal "strains" which disturb the balance within the unstable orthomolecules. One is shown here (at left) being symbolically "twisted" by the action of the field. The actual process is governed by quantum rules and the transition to the stable para structure is sudden. Another possible mechanism, for which the evidence is more definite at higher temperatures, is shown symbolically at the right. Here the orthomolecules dissociate as they are adsorbed on the catalyst surface, and then the atoms can recombine into a stable paramolecule as they are desorbed.

PARAHYDROGEN PRODUCTION

simplifies liquid hydrogen storage problem

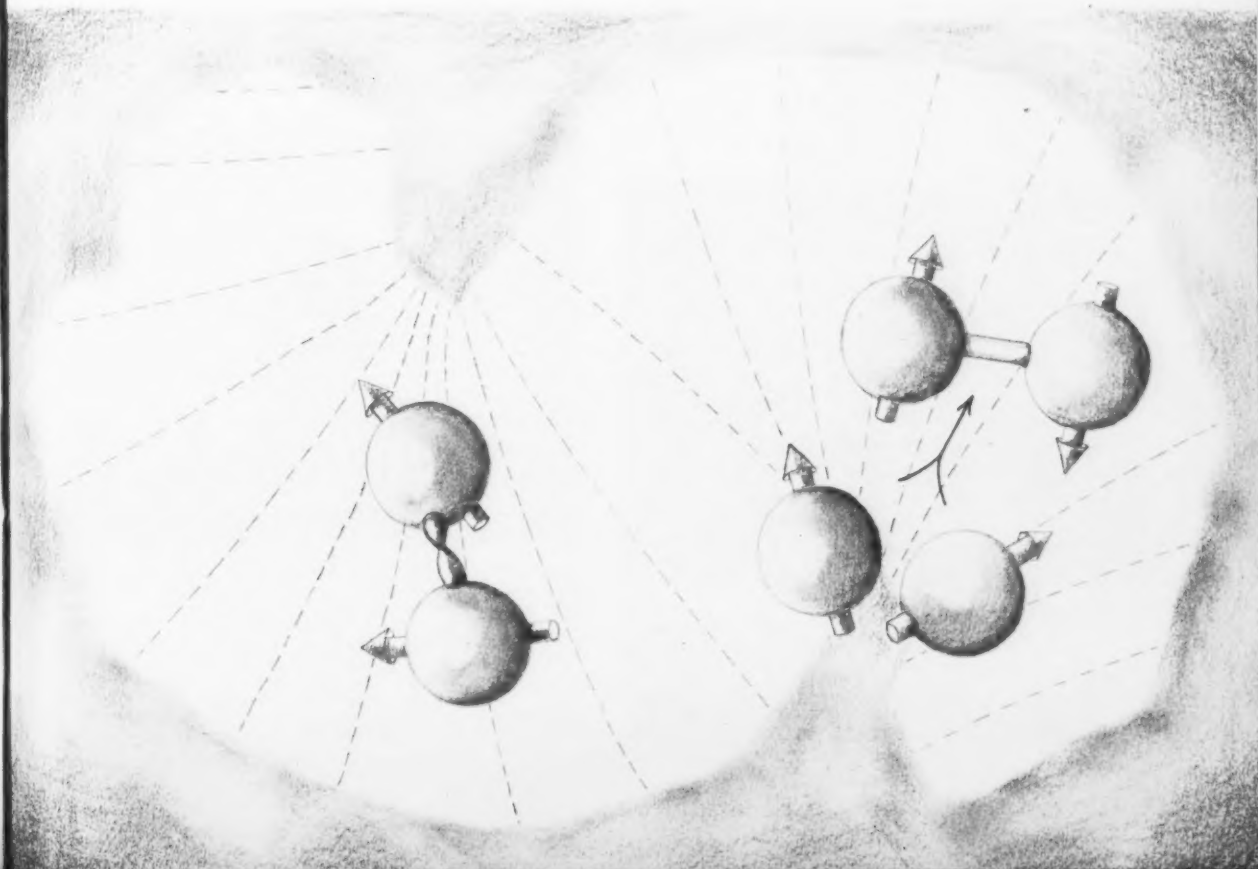
the number of ortho-to-para changes exactly equals the number of para-to-ortho changes. Thus the ratio of orthohydrogen to parahydrogen becomes fixed, and this equilibrium ratio depends on the temperature of the hydrogen.

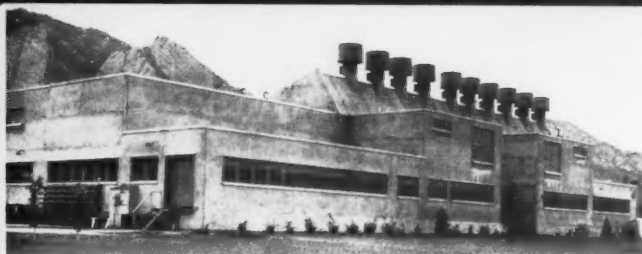
At room temperature, for example, so-called "normal" hydrogen at equilibrium contains 75 percent orthohydrogen and 25 percent parahydrogen. At the boiling temperature (-423°F), the equilibrium ratio shifts to 0.2 percent orthohydrogen and 99.8 percent parahydrogen. Thus any change in temperature of

the gas is accompanied by a change in the equilibrium ratio.

If normal gaseous hydrogen in equilibrium at room temperature is cooled rapidly to its liquefaction temperature, a fluid results which is in a highly unstable energy condition. That is, the conversion from orthomolecules to paramolecules does not take place fast enough to maintain the rapidly shifting equilibrium ratio between the two varieties.

Ordinary freshly liquefied hydrogen therefore contains a much greater fraction of orthohydrogen than





View of Liquefier Building at the Boulder Laboratories.

it will after reaching equilibrium. For this reason, the ortho-to-para conversion of molecules proceeds faster than the reverse para-to-ortho conversion. This means, of course, that energy is released within the liquid. This energy vaporizes some of the liquid even though the container insulation is perfect. It is therefore quite impossible to store ordinary unconverted liquid hydrogen efficiently unless a refrigerator is used to remove continuously the heat of ortho-to-para conversion.

The problem would be resolved if, while the hydrogen is cooling down in the liquefier (which is merely an efficient refrigerator), the ortho-to-para conversion could keep pace with the change in equilibrium ratio which occurs as the temperature goes down. This does not happen because each orthomolecule is "balanced," so to speak, in its unstable configuration and will remain so until some force influences one proton of the molecule more strongly than it does that proton's partner. If this happens, the disturbed proton will very likely "flip over" so that its spin orientation is opposite that of its partner, thereby forming a stable parahydrogen molecule.

The slow natural ortho-to-para conversion, which continues until eventually 99.8 percent of the liquid is parahydrogen, is caused by a process known as "self catalysis." This means that if two orthohydrogen molecules approach one another closely enough, their

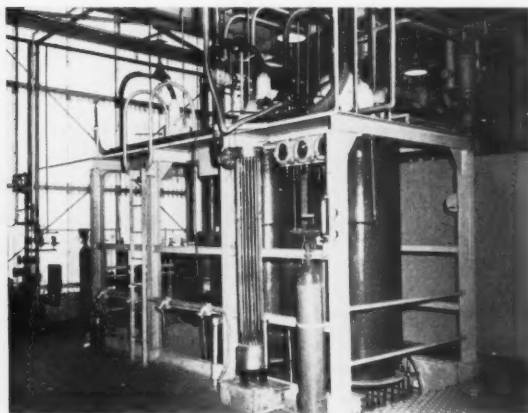
magnetic fields interact (orthohydrogen molecules being magnetic) and unbalance the molecules so that a reorientation of spins takes place. However, the frequency of these events is such that it takes about a month for normal 25 percent para liquid to convert to 90 percent para. The heat energy released during this month of self conversion is enough to boil away 6 percent of the original liquid.

Selecting a Catalyst

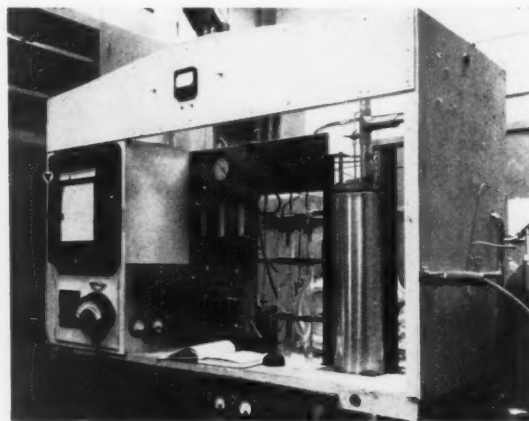
The conversion rate would be greatly accelerated if, while still in the liquefier, the hydrogen were to pass over a great many points of intense magnetic gradient so that each surplus orthomolecule would stand a good chance of having its unstable equilibrium unbalanced. This is precisely what the proper catalyst does.

For this, two things are essential: (1) A strong magnetic field, inhomogeneous on a scale of molecular dimensions, and (2) a physical structure which allows all of the hydrogen molecules to come into intimate contact with the magnetic centers. The first condition is met by choosing a material with high magnetic susceptibility, and the second (in the case of a solid catalyst) by obtaining an extremely fine porosity which results in a huge internal surface area. In addition, there is another mechanism that may play an important, if secondary, part (and for which the evidence is more definite at higher temperatures), which involves the dissociation and recombination of hydrogen molecules and atoms as they are adsorbed on and desorbed from the extended surface of the catalyst. For this mechanism, also, the hydrogen should be exposed to the maximum possible surface area of the catalyst.

Many investigators have searched for catalysts suit-



Purifier and final heat exchanger units of the 250-liter-per-hour parahydrogen liquefier. Ortho-to-para converters utilizing hydrous ferric oxide as the catalyst enter the process at 2 stages: Conversion to 51 percent para occurs in the gas phase at -331°F and conversion to 95 percent para takes place in the liquid phase at -422°F .



Apparatus for evaluating catalysts for converting ortho-to-parahydrogen. Normal or partially converted hydrogen is cooled by means of cryogenic baths, then passed at measured flow rates through the catalyst under test. Effectiveness of the catalyst is measured by the completeness of conversion to the low-temperature equilibrium. A gas analyzer based on differences in thermal conductivity measures and continuously records the para concentration of the emerging hydrogen.

able for promoting this conversion.¹ Workers at Los Alamos Scientific Laboratory succeeded in 1953 in modifying a 25-liter-per-hour hydrogen liquefier for the regular production of 85 percent parahydrogen. This achievement was followed shortly by the successful modification of the hydrogen liquefier at the Boulder Laboratories to produce 240 liters per hour of 90 to 95 percent liquid parahydrogen.

Concurrently with these developments, the cryogenic engineering laboratory in 1952 started a research program under the direction of D. H. Weitzel, sponsored by the AEC, to study and evaluate catalysts suitable for the production of liquid parahydrogen. W. V. Loebenstein of the surface chemistry laboratory in Washington joined the project for the first year of the work.

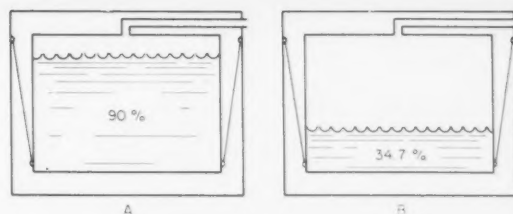
Hydrous ferric oxide was one of several catalyst materials suggested and prepared by Dr. Loebenstein. These catalysts, along with others prepared at Boulder, were evaluated for effectiveness in ortho-to-para conversion by Weitzel and coworkers. The most effective catalyst tested, by a considerable margin, was hydrous ferric oxide.

Hydrous ferric oxide results from the removal, through controlled heating, of entrained water from ferric hydroxide gel. The product thus obtained is hard and strong; and it has an available effective surface area, when measured by gas adsorption methods, of as much as 150 square meters per gram (about 16.8 acres per pound). Furthermore, since iron is ferromagnetic and therefore has very high magnetic susceptibility, it is not surprising that it has proved an unusually effective ortho-para conversion catalyst. Its high conversion efficiency permits the design of ortho-para converters about one-fortieth the size of those used in the early work at Los Alamos and the National Bureau of Standards. Thus the size of these installations used in connection with extremely large hydrogen liquefiers can be kept manageable.

Experiments have shown that conversion in the gas phase proceeds more slowly than in the liquid phase. Data now exist permitting the prediction of catalyst quantities required to do an efficient job of gas-phase, as well as liquid-phase, conversion.

The cryogenic engineering laboratory has also been doing research on materials and methods for improving liquid hydrogen storage Dewar design. Both high vacuum and evacuated powder insulation techniques² have been investigated, along with novel insulating support methods. The information has been widely applied by commercial fabricators of this type of equipment and highly efficient storage Dewars for liquid parahydrogen have resulted.

Container for liquid parahydrogen, capacity 1,300 gallons. The walls contain highly efficient evacuated powder insulation. Containers of this kind, without auxiliary refrigerators, were not practical before the development of ortho-para converters in hydrogen liquefiers. In unconverted liquid hydrogen, heat is generated internally by molecular changes, so that even perfect insulation will not prevent evaporation losses.



Illustrating the more efficient storage possible with liquid parahydrogen. The greater evaporation loss in "normal" hydrogen (75 percent orthohydrogen, 25 percent parahydrogen) is due to the heat generated when the unstable orthomolecules spontaneously change to the para form. By means of a highly effective catalyst it is possible to eliminate all but a small portion of the orthomolecules during the process of liquefying hydrogen. A: A well-insulated container of liquid parahydrogen after 10 days of storage. There has been a 10 percent loss due to heat leak through the insulation and supports. B: A well-insulated container of liquid normal hydrogen after 10 days of storage. A 10-percent loss has occurred due to heat leak through the insulation and supports and a 55.3-percent loss due to heat of spontaneous ortho-to-para conversion.

¹ For further technical details, see Iron catalyst for production of liquid parahydrogen, by D. H. Weitzel and O. E. Park, *Rev. Sci. Instr.* **27**, 57 (Jan. 1956); The regular production of 85 percent para liquid hydrogen, by E. R. Grilly, *Rev. Sci. Instr.* **24**, 899 (1953); The liquefaction and storage of partially converted liquid hydrogen, by E. R. Grilly, *Rev. Sci. Instr.* **24**, 1 (1953); The para-hydrogen conversion at paramagnetic surfaces, by H. S. Taylor and H. D. Diamond, *J. Am. Chem. Soc.* **55**, 2613 (1933).

² Powders for low-temperature insulation, *NBS Tech. News Bul.* **41**, 87 (June 1957).



Electron-Optical Study of Low-Density Gas Flow

IT IS NOT TOO DIFFICULT, for the relatively low altitudes at which conventional aircraft fly, to determine experimentally the behavior of the atmosphere as it streams around the craft. However, at densities corresponding to the rarefied regions of the upper atmosphere into which rockets are now penetrating, data on the aerodynamic behavior of gases—on the mass and velocity distributions of the gas molecules—are increasingly difficult to obtain. Existing methods for coping with this problem become progressively less sensitive as the density is reduced; eventually they fail altogether. Optical techniques, for example, become ineffective at such low densities because both the gradient of the index of refraction and the difference between the index of refraction of the gas and that of a perfect vacuum approach zero.

A promising laboratory technique for solving this problem has been developed by L. L. Marton, D. C. Schubert, and S. R. Mielczarek of the Bureau in a research program supported by the Office of Naval Research.¹ The method uses an electron-optical Schlieren technique to produce a photographic image of the gas stream. Because it depends on the scattering of electrons in collisions with individual gas molecules, this technique is more effective at much lower pressures. It is however necessary that the gas density in the region of interest be higher than that in the remainder of the apparatus, and this can be assured by modern vacuum technique.

The apparatus already constructed extends the range of pressures at which gas flow may be studied down to less than 10^{-5} mm of Hg (roughly, one one-hundred-millionth of normal atmospheric pressure). Thus far the apparatus has been used to study the distribution of particle density in beams of cadmium atoms. After other vapors are studied in the same way, attention will be given to beams of the permanent gases.

A modification of this equipment has been designed which will permit measurement of the velocity distribution in beam particles that have been reflected from a metallic obstacle. The modification uses a stroboscopic principle and is now in the early testing stage. The data it provides will be used to compute the coefficients of thermal accommodation and viscous slip that are of interest in the aerodynamics of artificial earth satellites and guided missiles.

Schlieren Technique

Basic to the Bureau's method is an electron-optical analog of the Schlieren light-optical technique. The latter is used, for example, in obtaining the familiar photographs of shock waves produced by projectiles. In the electron-optical version, a wide beam of electrons diverging from a point source is directed through the region of gas flow and then focused on a small metal stop. If the gas stream were absent (and no other molecules were present), all of the electrons would be collected by the stop. However, electrons scattered

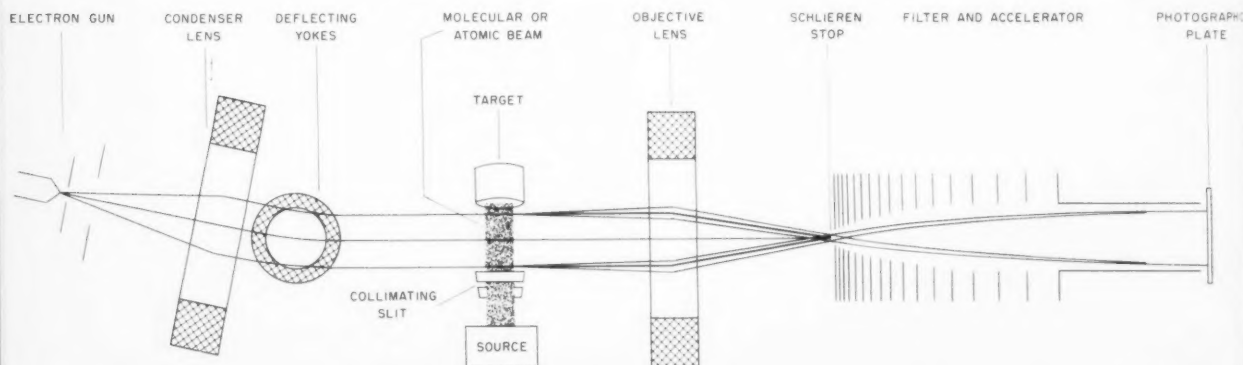
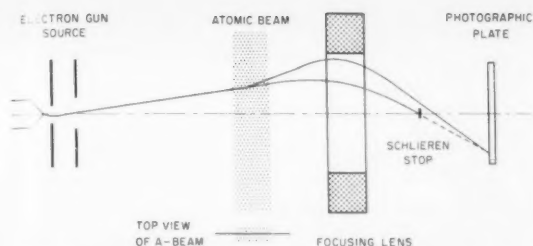


Diagram of instrument developed for studying gas flow at low pressures such as exist in the upper atmosphere. The filter and accelerator unit, consisting of a series of flat metal rings at various electrical potentials, (1) presents a potential barrier to secondary electrons knocked out of the Schlieren stop and which would otherwise fog the photographic plate, and (2) lets through the image-forming electrons and "post-accelerates" them to produce a more intense image. The axis of the electron gun is at an angle with the main instrument axis in order to keep light from the gun filament away from the photographic plate; electrons are guided around the bend by a magnetic deflector. Other features are the special attention to vacuum technique and the balancing out of spherical aberration produced by the various magnetic and electrostatic fields. Experiments thus far have used a cadmium vapor beam generated in an oven (source) and condensed on a metal target kept at 77° K by liquid nitrogen.



Principle of electron-optical Schlieren photography of a gas stream (molecular or atomic beam) at very low pressures. A divergent beam of electrons crosses the path of the gas stream, and electrons that pass through without collision are focused onto a small metal disk, the Schlieren stop. On the other hand, electrons scattered by the gas particles overshoot the stop and are brought to a focus on a photographic plate. The density of electrons striking a given point on the plate is proportional to the average gas particle density along the electron trajectory.

by the gas molecules miss the stop and are recorded on a photographic plate located in the image plane conjugate to the midplane of the streaming gas. The advantage of the Schlieren technique is that it separates the scattered electrons from the nonscattered ones, and so prevents the latter from clouding the photographic image.

Electrons scattered from a given point in the gas stream are brought to a common focus on the photographic plate by means of a magnetic lens. The focus is sharpest for points in the midplane of the stream and does not depart too much from the optimum if the stream width is kept within reasonable limits. Under such circumstances the density of electrons impinging at any point on the plate is approximately proportional to the average gas density (or to the line integral of the gas density) along the electron trajectory.

Instrumental Development

The problem of designing the optics of this type of instrument to provide simultaneously high sensitivity, sharp focus, and freedom from image distortion shares a number of features with the corresponding problems

Instrument for studying gas flow at very low pressures. Starting at upper right, the main components visible are: The electron gun (in transparent cylinder); magnetic condensing lens (black-edged drum); assembly containing oven, collimating slit, and condensing target for gas beam; main focusing lens (black-edged drum); filter and accelerator unit; and photographic plate holder and air lock (rectangular assembly). Scientist is attaching high-potential lead to filter-accelerator unit. For preliminary adjustments, the photographic plate can be replaced by a fluorescent screen which can be viewed through the circular opening (lower left). Auxiliary vacuum pump and low-temperature equipment are not shown. The wooden structure on which the scientist's left hand is resting contains the coils that compensate for the earth's magnetic field. These are necessary because the energy of the electron beam is so low that the earth's magnetic field will cause the beam to be deflected from a straight-line path.

in electron microscopy and cathode-ray tube development. Experience has shown, however, that it is also sufficiently different from these areas to constitute a separate discipline.

In the simple instrument described above, the energy of the exploring electrons is generally from 1 to 2 kev. This provides a convenient range of scattering angles, but it also produces an extremely weak photographic image. This problem is met by accelerating the electrons to about 15 kev after they have passed the Schlieren stop. It is found that such "post-acceleration" does provide the desired image intensity, but it also causes several additional difficulties that have had to be overcome.

One difficulty is that secondary electrons generated at the Schlieren stop are attracted to the photographic plate by the electrostatic post-acceleration field and provide an extraneous background. This was eliminated by inserting a decelerating field between the post-acceleration field and the Schlieren stop. The new field can be made strong enough to repel all of the secondary electrons while being easily penetrable by electrons scattered from the gas beam.

Now the electrostatic fields thus added to the basic Schlieren arrangement constitute a lens that must be taken into account if a sharp image is to be obtained. Electrostatic lenses usually suffer from a great amount of spherical aberration, which results in serious image distortion under the conditions of the present experiment. This was minimized by reducing the focusing action of the added deceleration and acceleration fields to a minimum, since the effect of the spherical aberration

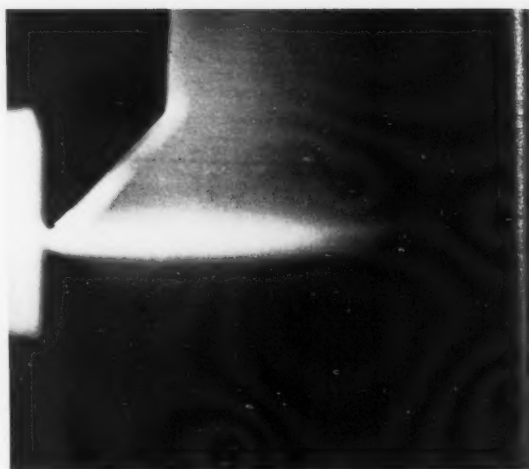


Photograph of cadmium vapor beam at pressure of about 10^{-4} mm of Hg made with electron-optical Schlieren instrument. The cadmium vapor, produced in an oven is collimated by the slit (left) into a ribbon-shaped beam and condenses on the target wall (right) which is maintained at 77° K by liquid nitrogen.

tion is correspondingly decreased. It was then possible, by careful design, to cancel the remaining "pincushion" distortion with distortion of the opposite sign produced by the main focusing coil.

The gas stream is generated by the now familiar molecular-beam technique. Cadmium metal is evaporated in an oven fitted with a narrow rectangular slit through which the molecules can escape; and the rate of escape is kept sufficiently low so that the molecules travel in unobstructed straight-line paths. A collimating slit several centimeters away from the oven then defines a ribbon-shaped beam of molecules essentially free of lateral motion. The axis of the electron beam is directed parallel to the plane of the ribbon and perpendicular to the direction of advance of the molecules. Finally, after passing through the electron beam, the cadmium molecules are condensed on a surface at liquid-nitrogen temperature (77° K).

A second instrument is now being designed to apply a proposed technique for stroboscopic operation. The cadmium beam is cut into short pulses by means of a radially slotted circular disk rotating at 8000 rpm. The electron beam is also pulsed; it is cut off at all times except for an interval of a few tenths of a microsecond starting about 10 microseconds after the arrival of each pulse at a metal target. In this way a stroboscopic picture of the gas density is produced. Because the distance of any molecule from the target is equal to the product of the molecule's velocity and the chosen time interval (about $10 \mu\text{sec}$) since it struck the target, the picture also exhibits the distribution in velocity of the reflected molecules.



The instruments developed at the Bureau for studying gas streams at very low pressures have evolved step by step from the relatively simple electron analog of the optical Schlieren arrangement. The basic electron Schlieren instrument itself was developed in several years of research in which the Schlieren technique was applied to the mapping of small electrostatic and magnetic fields inaccessible to other kinds of measurement.²

¹Electron optical image of an atomic beam, by L. Marton, D. C. Schubert, and S. R. Mielczarek, *J. Appl. Phys.* **27**, 4 (April 1956).

²Electron-optical Schlieren effect, *NBS Tech. News Bul.* **32**, 82 (July 1948); Electron-optical shadow method, *NBS Tech. News Bul.* **33**, 107 (Sept. 1949); Electron-optical mapping of the space-charge field in a magnetron, *NBS Tech. News Bul.* **34**, 57 (May 1950).

Viscometer Calibration Discontinued

EFFECTIVE January 1, 1958, the National Bureau of Standards will discontinue calibration of viscometers. This action is in line with the Federal Government's general policy of withdrawing from activities that can be carried on by private industry. It will permit the Bureau to devote more of its resources toward meeting the demands of science and industry for new and more accurate standards.

Viscometers are widely used in industry and science to observe and study the flow characteristics of non-rigid materials. However, most users of these instruments now carry out the calibrations in their own laboratories using viscosity standards available from the National Bureau of Standards, the American Petroleum Institute, or elsewhere. Calibration by the user has the advantage that the effects of any slight peculiarities of operating techniques and accessory equipment tend

to cancel out when they are the same for both the calibration and the measurements of unknowns. Inquiries addressed to those who have used the service in recent years, and to other interested parties, have brought forth no substantial objections to discontinuance of the service.

Of the many types of viscometers in use, only a few have been calibrated by the Bureau. In recent years these have included only the Saybolt, the Modified Ostwald, and the suspended level types. In 1956, calibration of Saybolt viscometers was discontinued as a logical result of the abandonment of the Master Saybolt viscometers as standards. Requests for calibration of the glass capillary tube instruments have been limited almost entirely to the Modified Ostwald (Fenske or Cannon-Fenske) instruments, and there has been little demand for this service in the last few years.

Controlled Slack Quenching of Impact Specimens

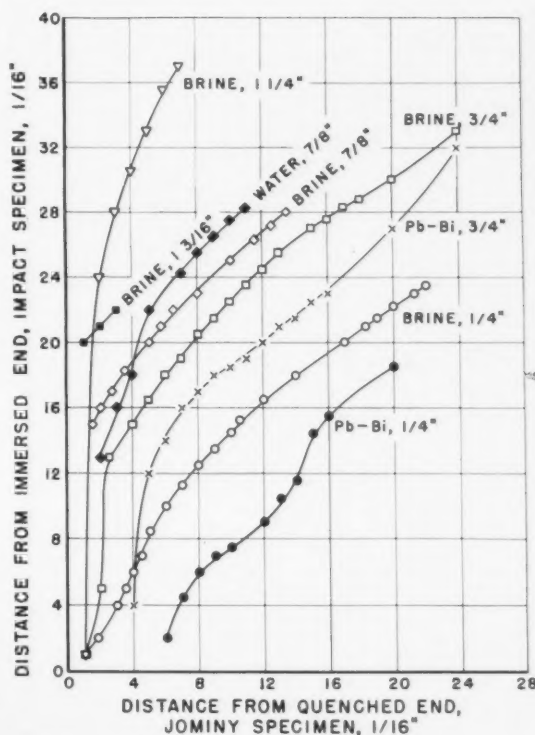
A SLACK-QUENCHED STEEL is one that is cooled too slowly from its hardening temperature to insure maximum hardness throughout. This effect cannot be avoided in unalloyed steel parts having large cross sections because heat cannot be withdrawn from the interior fast enough to effect complete hardening. Thus microstructure and mechanical properties vary continuously throughout the metal.

The Bureau has recently developed an accurate method for measuring the effect of slack quenching on the impact resistance of steel. Devised by M. R. Meyerson and S. J. Rosenberg of the thermal metallurgy laboratory, the procedure uses a Charpy (V-notch) impact specimen which has been immersion end quenched.¹ The quenching forms a series of planes having different but predictable microstructures and hardnesses depending on their distance from the quenched end. The depth of immersion and type of quenching medium used are predetermined from data obtained from an end-quenched Jominy specimen of the steel under study.

Until now there has been little information on the properties of slack-quenched steels. Consequently, rather than risk the unknown, manufacturers often substitute deep hardening alloy steels for the less expensive carbon steels. The Bureau's method of controlled slack-quenching should help to determine in what cir-



An experiment in which an impact specimen, just removed from furnace, is held at opening in quenching fixture. Second specimen (left) is end-immersed in brine. Metal straps fasten the steel plate in position above quenching bath.



Correlation between points of equal hardness on end-quenched Jominy specimens and end-immersed impact specimens of the same steel. The plotted points represent locations of equal hardness and similar microstructure.

cumstances slack-quenched steels may be used. The method should lead to a broader understanding of the impact properties of steels as affected by microstructural variations, and may contribute to important savings in critical materials by reducing overdesign.

It was reasoned that impact specimens having slack-quenched structures might be prepared in a manner similar to that of Jominy specimens. A Jominy specimen is hardened by a jet end quench. In theory it contains an infinite number of parallel planes and, assuming no surface cooling, each plane is cooled at a constant rate decreasing in speed with increasing distance from the quenched end. As a result, each plane has a different hardness and microstructure. A series of quenching and hardness tests were made on end-immersed impact specimens and Jominy specimens of the same steels. The microstructures and hardness existing at selected distances from the quenched ends were correlated. The data revealed a distinct relationship between hardness and structure at specific planes

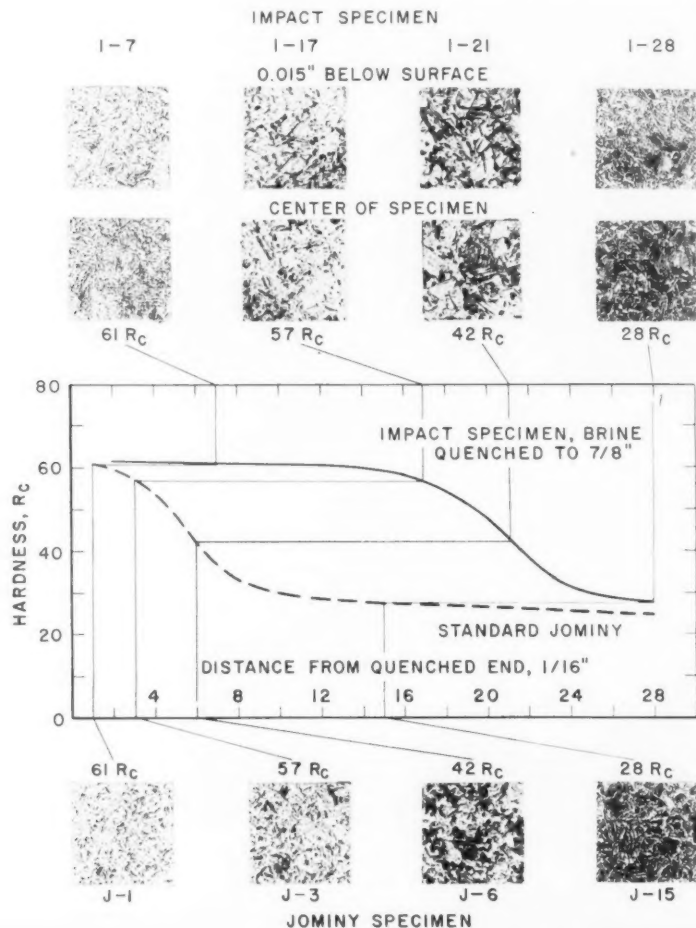
in the two types of specimens. These data have been reduced to graphical form for easy reference.

In studying impact properties of slack-quenched structures, a standard Jominy bar of the steel under investigation is first end quenched according to ASTM specifications. A hardness survey along the length of the specimen is correlated with the microstructures. Once the desired hardness or structure is located in the Jominy bar and the distance from the quenched end established, the graph may be used. For example, one might want to study the impact properties of a specimen having the microstructure that exists $\frac{8}{16}$ of an inch from the quenched end of a Jominy bar. Reference to the graph indicates that an impact specimen immersed to $\frac{7}{8}$ in. in brine will have the desired hardness and structure at $\frac{23}{16}$ in. from the immersed end. If the specimen is immersed only $\frac{3}{4}$ in., the desired structure will appear at $\frac{20}{16}$ in. from the quenched end. In this case, either immersion depth may be used since the notch used in impact tests must be located close to the center of the specimen and at least 1.08 in. from the quenched end.

After quenching, the specimens may require a low temperature stress relief (250° F) to inhibit subsequent cracking. Then the specimens are ground equally on all sides to remove any scaling and decarburization that may have occurred. A hardness survey made on one face locates the desired slack-quenched structure, and a standard V-notch is cut into the specimen at that point. Finally the ends of the specimen are cut off at a distance of 1.08 in. on each side of the notch. The impact resistance at that particular plane may then be determined by the Charpy impact test. Numerous hardness and metallographic surveys from center to surface of impact specimens, after removal of the decarburized layer, have established the uniformity of hardness and microstructure in any plane above the immersion level and parallel to the quenched end.

In making the impact specimens, they are first rough machined to a size slightly larger than the standard impact specimen to allow for scaling and decarburization during heat treatment and to allow some latitude for locating the notch. One end of the specimen is

Hardenability curves and microstructures at equal hardness levels on an impact specimen and a standard Jominy specimen. The microstructures of both are the same at equal hardness levels. Note that the microstructures of the impact specimen are uniform from just below the surface to the center.



drilled and tapped to accommodate a 1/4-in. length of a 1/2-20 screw, 2 in. long. A washer, locked in a selected position by two nuts, supports the specimen in a quenching fixture. Thus, a predetermined length of the specimen may be immersed vertically in a brine, water, or other quenching medium. The fixture is made of 1/4-in. steel plate with drilled holes for eight specimens.

The method is suitable for the study of tempered as well as untempered slack-quenched structures. In such studies a predetermined tempering treatment is given the specimen after locating the selected slack-quenched hardness on the untempered specimen. After temper-

ing, the notch is cut and the impact strength may be determined.

Data obtained by the Bureau's method have established quantitatively the detrimental effect of various degrees of slack quenching on the impact properties of triple alloy steels (those containing small amounts of nickel, chromium, and molybdenum). The influence of varying carbon and alloy contents on the impact properties of slack-quenched structures has also been determined quantitatively.

¹ Impact properties of slack-quenched steel, by M. R. Meyerson and S. J. Rosenberg, *J. Research NBS* **59**, 273 (1957) RP2799.

Publications of the National Bureau of Standards

Journal of Research of the National Bureau of Standards, Volume **59**, No. 3, September 1957 (RP2783 to RP2791 incl.), 60 cents. Annual subscription \$4.

Technical News Bulletin, Volume **41**, No. 9, September 1957, 10 cents. Annual subscription \$1.

Basic Radio Propagation Predictions for December 1957. Three months in advance. CRPL-D 157. Issued September 1957. 10 cents. Annual subscription \$1.

Research Papers

Journal of Research, Volume **59**, No. 3, September 1957. 60 cents.

RP2783. A computation of cyclic cubic units. Harvey Cohn and Saul Gorn.

RP2784. Estimation of the frequencies of thin elastic plates with free edges. Tosio Kato, Hiroshi Fujita, Yoshimoto Nakata, and Morris Newman.

RP2785. A thermochemical study of the reaction of calcium hydroxide, silica gel, and water. Edwin S. Newman.

RP2786. On some expansions for Bessel integral functions. F. Oberhettinger.

RP2787. Table of the first moment of ranked extremes. Julius Lieblein and Herbert E. Salzer.

RP2788. An approximate expression for gamma-ray degradation spectra. U. Fano and Ann T. Nelms.

RP2789. Some infrared bands of deuterium sulfide. Harry C. Allen, Jr., Earle K. Plyler, and L. R. Blaine.

RP2790. Some effects of low temperatures and notch depth on the mechanical behavior of an annealed commercially pure titanium. Glenn W. Geil and Nesbit L. Carwile.

RP2791. Determination and use of the sag point as a reference point in the heating of glasses. Sam Spinner, Given W. Cleek, and Edgar H. Hamilton.

Circulars

C562. Supplement 1. Bibliography of research on deuterium and tritium and compounds 1953-1954. Virginia R. Johnson, Lawrence M. Brown, and Abraham S. Friedman. 25 cents.

Building Materials and Structures Reports

BMS149. Combustible contents in buildings. S. H. Ingberg, John W. Dunham, and James P. Thompson. 20 cents.

Miscellaneous Publications

M221. Hydraulic research in the United States. 1957. \$1.50.

Publications in Other Journals

An observation of audio-frequency electromagnetic noise during a period of solar disturbance. J. M. Watts. *J. Geophys. Research.* (Editorial Office, 5241 Broad Branch Rd. NW., Washington 15, D. C.) **62**, No. 2, 199-206 (June 1957).

Changes in agar-agar type duplicating material and agar-agar on heating and storage. Peter M. Margetis and William C. Hansen. *J. Am. Dental Assoc.* (222 E. Superior St., Chicago 11, Ill.) **54**, 737-745 (June 1957).

Design and performance of a portable infiltration meter. Carl W. Coblenz and Paul R. Achenbach. *Heating, Piping Air Conditioning.* (Keeney Publishing Co., 6 N. Michigan Ave., Chicago 2, Ill.) **29**, No. 7, 155-158 (July 1957).

Techniques for electroforming of precision wave-guide components in the millimeter wave-length. A. A. Feldmann. *Rev. Sci. Instr.* (The American Inst. of Physics, 57 E. 55th St., New York 22, N. Y.) **28**, 295-296 (Apr. 1957).

Transmittance of infrared energy by glasses. Francis W. Glaze. *Am. Ceram. Soc. Bull.* (4055 N. High St., Columbus 14, Ohio) **34**, No. 9, 291-294 (Sept. 1955).

Transistor beta tester. G. Franklin Montgomery. *Electronics.* (Subscription Service, McGraw-Hill Book Co., Inc., 330 W. 42d St., New York 36, N. Y.) **30**, No. 5, 198 (May 1957).

The transient behavior of the electromagnetic ground wave on a spherical earth. James R. Wait. *Inst. Radio Engrs. on Antennas and Propagation.* (American Inst. of Electrical Engineers, 33 W. 39th St., New York 18, N. Y.) **AP-5**, No. 2, 198-202 (Apr. 1957).

The precise measurement of the infrared spectra of molecules of the atmosphere. Earle K. Plyler and Eugene D. Tidwell. *Molécules dans les Astres.* (Institut d'astrophysique, Cointesclassin, Belgique) **tone XVIII** 426-450 (1957).

The clamp-type alternating-current microammeter. G. Franklin Montgomery and Carroll Stansbury. *Am. Inst. Elec. Engrs.* (American Institute of Electrical Engineers, 33 W. 39th St., New York 18, N. Y.) Paper No. 57114 (1957).

Adsorption of carbon-14 dextran to human blood platelets and red blood cells, in vitro. S. Rothman, E. Adelson, A. Schwebel, and R. D. Langdell. *J. Blood Transfusion and Immunohaematology.* (Basel, Switzerland) **2**, No. 2, (1957).

ν_3 band of methane. Harry C. Allen, Jr., and Earle K. Plyler. *J. Chem. Phys.* (American Inst. of Physics, 57 E. 55th St., New York 22, N. Y.) **26**, No. 4, 972-973 (Apr. 1957).

Commutativity in finite matrices. Olga Tausky. *Amer. Math. Monthly.* (The Mathematical Association of America, University of Buffalo, Buffalo, N. Y.) **64**, No. 4, (Apr. 1957).

Early history and development of building codes. James P. Thompson. *B. O. C. A. News.* (Building Officials Conference of America, Inc., 110 E. 42d St., New York 17, N. Y.) **6**, No. 1, (Jun. 1957).

Electronic averaging device for the adherometer. A. G. Roberts and R. S. Pizer. *ASTM Bulletin.* (American Society for Testing Materials, Philadelphia 3, Pa.) No. 221, 53-58 (Apr. 1957).

Luminous reaction between carbon monoxide and atomic nitrogen. Herbert P. Broida and Donald F. Heath. *J. Chem. Phys.* (American Inst. of Physics, 57 E. 55th St., New York 22, N. Y.) **26**, No. 5, 1352 (May 1957).

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NBS Publications (continued)

- Methods for evaluation of rotating diamond-abrasive dental instruments. Jack L. Hartley, Donald C. Hudson, W. T. Sweeney, and George Dickson. *J. Am. Dental Assoc.* (222 E. Superior St., Chicago 11, Ill.) **54**, 637-644 (May 1957).
- Noise in composition resistors. George T. Conrad, Jr. *Proc. Natl. Electronics Conf. (National Electronics Conference, Inc., 84 East Randolph St., Chicago, Ill.)* **10**, (Feb. 1955).
- Pitfalls in computation. Irene A. Stegun and Milton Abramowitz. *J. Soc. Indust. Appl. Math. (Siam Box 7541, Philadelphia 1, Pa.)* **4**, No. 4, (Dec. 1956).
- The impedance of a wire grid parallel to a dielectric interface. James R. Wait. *IRE Trans. on Microwave Theory and Tech. (The Institute of Radio Engineers, 1 E. 79th St., New York 21, N. Y.)* **MTT-5**, No. 2, 99-102 (Apr. 1957).
- 45-year corrosion study. Melvin Romanoff. *Petrol. Engr. (Petroleum Engineer Publishing Co., 800 Davis Bldg., Dallas 2, Texas)* **29**, No. 3 and 4, 615-635 (Mar. and Apr. 1957).
- The impact-absorbing capacity of textile yarns. J. C. Smith, F. L. McCrackin, and H. F. Schiefer. *ASTM Bulletin. (American Society for Testing Materials, Philadelphia 3, Pa.)* **220** (Feb. 1957).
- Vacuum-insulated transfer tube. R. B. Jacobs and R. J. Richards. *Rev. Sci. Inst. (American Inst. of Physics, 57 E. 55th St., New York 22, N. Y.)* **28**, 291-292 (Apr. 1957).
- Diffusion of particles with memory. Peter L. Bender. *Proc. Natl. Acad. Sci. (Univ. of Chicago Press, 5750 Ellis Ave., Chicago 37, Ill.)* **43**, No. 5, 412-416 (May 1957).
- Galvanomagnetic effects in n-type InSb at 4.2° K. H. P. R. Frederikse and W. R. Hosler. *Can. J. Phys. (Division of Administration, National Research Council, Ottawa 2, Can.)* **34**, 1377-1378 (1956).
- Head regulator for cutoff valve. Leonard Bean. *Anal. Chem. (American Chemical Society, 1155 16th St. NW., Washington 6, D. C.)* **29**, No. 6, 987 (June 1957).
- Introduction to the VLF papers. James R. Wait. *Proc. I. R. E. (Inst. of Radio Engineers, Inc., 1 E. 79th St., New York 21, N. Y.)* **45**, No. 6, 739-740 (June 1957).
- Mathematics.—A note on values of a quadratic form. M. Marcus. *J. Wash. Acad. (Custodian and Subscription Mgr. of Publications, U. S. National Museum, Washington 25, D. C.)* **47**, No. 4, 97-99 (Apr. 1957).

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- On standard methods of measurement in architectural acoustics. Richard V. Waterhouse. *J. Acoust. Soc. Am. (American Inst. of Physics, Prince and Lemon Sts., Lancaster, Pa.)* **29**, No. 5, 544-547 (May 1957).
- On prediction of system performance from information on component performance. Joan R. Rosenblatt. *Proc. Western Joint Computer Conf. (Inst. Radio Engrs. 1 E. 79th St., New York 21, N. Y.)* 85-94 (Feb. 1957).
- Relation between roughness of interface and adherence of porcelain enamel to steel. J. C. Richmond, D. G. Moore, H. B. Kirkpatrick, and W. N. Harrison. *Inst. Vitreous Enamellers Ltd. Bull. (J. D. Gardom, Secy., Inst. of Vitreous Enamellers, Ripley, Near Derby, England)* **7**, No. 5, 69-79 (May 1957).
- A service for the Nation's technology. Allen V. Astin. *Mag. of Standards. (American Standards Association, Inc., 70 East 45th St., New York 17, N. Y.)* **28**, No. 7, 196-199 (July 1957).
- Stabilization of free radicals at low temperatures. Herbert P. Broida. *Ann. N. Y. Acad. Sci. (Secy. New York Academy of Sciences, 2 E. 63d St., New York 21, N. Y.)* **67**, No. 9, 530-545 (May 1957).
- The attenuation vs frequency characteristics of VLF radio waves. James R. Wait. *Proc. I. R. E. (Inst. of Radio Engineers, Inc., 1 E. 79th St., New York 21, N. Y.)* **45**, No. 6 (June 1957).
- The galvanic corrosion theory for adherence of porcelain enamel ground coat to steel. D. G. Moore, J. W. Pitts, J. C. Richmond, W. N. Harrison. *Inst. Vitreous Enamellers Ltd. Bull. (Inst. of Vitreous Enamellers, Ripley, Near Derby, Eng.)* **7**, No. 4 (Mar. 1957).
- The geometrical optics of VLF sky wave propagation. J. R. Wait and A. Murphy. *Proc. I. R. E. (Inst. of Radio Engineers, Inc., 1 E. 79th St., New York 21, N. Y.)* **45**, No. 6, 756-760 (June 1957).

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